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UNITED STATES DEPARTMENT OF THE INTERIOR

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ILLUSTRATIONS

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

bpm	breath per minute	$g \cdot cm^{-3}$	gram per cubic centimeter
cm	centimeter	L	liter
cm^2	square centimeter	L/min	liter per minute
cm^3/min	cubic centimeter per minute	$mol \cdot cm^{-3}$	mole per cubic centimeter
$cm^3 \cdot mol^{-1}$	cubic centimeter per mole	$mol \cdot cm^{-3} \cdot s^{-1}$	mole per cubic centimeter per second
$cm \cdot s^{-1}$	centimeter per second	pct	percent
$cm^3 \cdot s \cdot mol^{-1}$	cubic centimeter second per mole	$rad \cdot s^{-1}$	radian per second
g	gram	s	second

MATHEMATICAL MODEL OF ABSORPTION OF CARBON DIOXIDE BY RESCUE BREATHING APPARATUS SCRUBBER

By John C. Edwards[1]

ABSTRACT

The Bureau of Mines developed a mathematical model for analysis of the impact of scrubber bed length, porosity, and gas flow rate on the absorption of CO_2 in a breathing apparatus. The model accounts for the decrease in available absorbent through chemical conversion. The predicted efflux of CO_2 from a canister containing LiOH compared favorably with measured values reported elsewhere. It was determined from a computational study that the time for breakthrough of CO_2 at a prescribed level is nearly directly proportional to bed length and inversely proportional to gas flow and porosity.

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INTRODUCTION

The safe utilization of a closed-circuit mine rescue breathing apparatus is dependent upon the efficient absorption of expired CO_2 that passes through a scrubber. The scrubber will consist of a hydroxide of a metal such as Na, Li, or Ca, and reside in a canister that is an integral part of the breathing apparatus. The design of the canister will be determined by consideration of the breathing flow resistance, absorption efficiency, and duration of the active absorption capacity. Physical properties of the absorbents were reported by Markowitz (1).[2]

Bernard, Kyriazi, and Stein (2) studied the effectiveness of CO_2 scrubbers. They monitored the CO_2 efflux from the scrubbers used in rescue breathing apparatuses through which passed compressed air containing 3.5 pct CO_2. They found that the effectiveness of the scrubber varied according to canister design and metal hydroxide absorbent used. It is the purpose of this report to present a mathematical model that can be used to ascertain the significance of factors that contribute to an efficient scrubber. In particular, bed length, gas flow rate, and bed porosity are evaluated as contributors to the absorption efficiency of LiOH. The bed porosity is determined by the volume and mass of the bed, as well as the particle porosity.

Prediction methods have involved both the development of mathematical models and the application of empirical expressions that are fitted in a statistical manner to the observed data. The former approach has been developed by Danby, Davoud, Everett, Hinshelwood, and Lodge (3), Davis and Kissinger (4), and Houston, Bailey, and Kumar (5). The latter approach was utilized by Boryta and Maas (6) in the analysis of CO_2 absorption by a portable life support system.

Boryta and Maas (6) examined the influence of the controllable quantities--lineal gas velocity, bed length, stoichiometry, temperature, and CO_2 inlet concentration--on the absorption capacity and CO_2 breakthrough time of a canister containing LiOH. They reported that the absorption capacity of the LiOH, i.e., the volume of CO_2 absorbed per unit time, depended primarily upon the gas velocity and bed length, with only minor dependence upon temperature and relative humidity, suggesting that the bed dynamics are more important than the chemical kinetics. In their study of breakthough time of CO_2 through the absorbent bed, they found using a regression analysis that the breakthrough time depended primarily upon the gas velocity, bed length, CO_2 inlet concentration, and their interaction. The breakthrough time is the time required for the CO_2 concentration in the effluent gas from the canister to reach a specified limit.

Davis and Kissinger (4) modeled the absorption of CO_2 by LiOH using concentration transport equations with a depletion term that depends upon the product of the available concentrations of CO_2 and LiOH. A premise for their calculation was that the time rate of change of the CO_2 concentration at a fixed location was much less significant than the convective flow of the CO_2. With this approximation for constant unidirectional flow, they were able to analytically evaluate the absorbent bed's average CO_2 efflux and the amount of the bed that had been used in the absorption process. Their model proved useful for analyzing the absorption of constant-flow CO_2 by LiOH beds.

Houston, Bailey, and Kumar (5) have shown that the introduction of a modified step function term in the concentration transport equations was required to reasonably simulate the CO_2 effluent concentration. They demonstrated through a comparison of predicted and measured values of CO_2 concentration that passed through $Ca(OH)_2$ that the modified step function properly accounted for the drop in reactivity after a definite amount of absorbent had been converted to carbonate.

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[2]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

These models (4-5) are applicable to constant-flow conditions in which the CO_2 transport dominates the nonsteady rate of change of the CO_2. In experimental studies of the CO_2 absorption capacity of rescue apparatuses, the gas flow rate will not be constant, but can be expected to vary in a manner characteristic of a miner's expiration. It is observed from the studies of Silverman and Billings (7) that the breathing patterns of subjects wearing protective respiratory devices that add external resistance to breathing have an approximately sinusoidal shape. The model presented in the following section, will permit inclusion of a time-dependent gas flow rate.

The model can be used in conjunction with the model presented in Information Circular 9063 (8) to describe the utilization of the absorbent by a miner in egressing from a mine. As the miner moves along an escape path through a mine network, the miner's breathing rate will vary in response to the stress associated with a mode of travel.

MODEL

The absorbent bed consists of a random distribution of pellets within a specific size range. Instead of focusing on the reaction and diffusion processes in a single pellet as was done by Ramachandran and Smith (9), a global model of an absorbent bed is utilized. Figure 1 shows the bed into which gas containing a specific concentration of CO_2 enters. The walls are assumed not to affect the gas flow. The molar concentrations C_1 and C_2 of the CO_2 and the absorbent are determined from a pair of coupled transport equations. Assumptions made in the construction of the transport equations are (1) the porosity is constant throughout the bed, (2) temperature effects are ignored, (3) moisture is not accounted for explicitly, and (4) diffusion is not significant. The values of C_1 and C_2 at a distrance x from the entrance to the bed at time t are determined from the following transport equations:

$$\varepsilon\left(\frac{\partial C_1}{\partial t} + u\,\frac{\partial C_1}{\partial x}\right) = -r_1 \qquad (1)$$

and

$$\frac{\partial C_2}{\partial t} = -r_2, \qquad (2)$$

where u is the interstitial gas velocity, r_1 is the absorption rate of CO_2, and r_2 is the rate of reaction rate of the absorbent. The additional assumptions that the gas diffusion effects are less important than the absorption process and that CO_2 is a small percentage of the total gas were made in equation 1. For the purpose of this report, LiOH is the absorbent and $r_2 = 2r_1$. Equations 1 and 2 reduce to those of Houston, Bailey, and Kumar (5) when the gas velocity is constant and the time rate of change of the CO_2 concentration at a fixed location is negligible compared to the convective transport of the CO_2.

Equations 1 and 2 can be rewritten in dimensionless form, and the interstitial velocity u is related to the superficial gas velocity v by the relationship

$$v = \varepsilon u. \qquad (3)$$

The dimensionless form of equations 1 and 2 is

$$\varepsilon\,\frac{C_1{}^{(0)}}{C_2{}^{(0)}}\,\frac{\partial \chi}{\partial \tau} + f(x,t)\,\frac{\partial \chi}{\partial \zeta} = -R, \qquad (4)$$

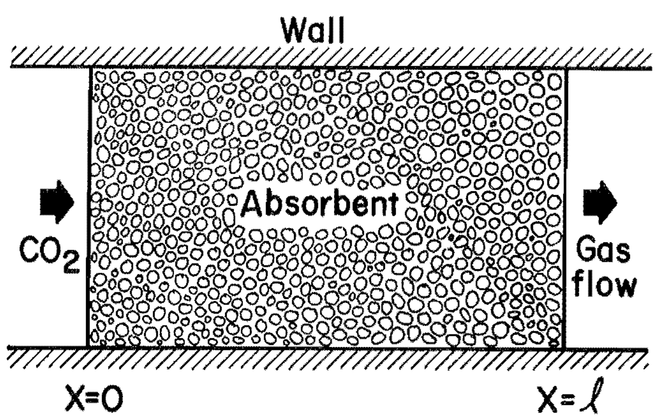

FIGURE 1.—Schematic of absorbent bed. X = distance from entrance of bed.

$$\frac{\partial \rho}{\partial \tau} = -2R, \tag{5}$$

$$R = \ell r_1/(voC_1{}^{(0)}), \tag{6}$$

$$t_1 = \ell C_2{}^{(0)}/(voC_1{}^{(0)}), \tag{7}$$

$$\tau = t/t_1, \tag{8}$$

$$\zeta = x/\ell, \tag{9}$$

$$v = vo\ f(x,t), \tag{10}$$

$$\chi = C_1/C_1{}^{(0)}, \tag{11}$$

and

$$\rho = C_2/C_2{}^{(0)}. \tag{12}$$

$C_1{}^{(0)}$ is the CO_2 concentration at the inlet, and $C_2{}^{(0)}$ is the initial absorbent concentration. In the model application presented here, $C_1{}^{(0)}$ remains constant to simulate a dead space that would adjoin the canister in a breathing apparatus. This is a boundary condition that can be readily changed. The spatial and temporal variation of the velocity are specified by the user and expressed by $f(x,t)$.

The reaction rate R is constructed in the manner prescribed by Houston, Bailey, and Kumar (5):

$$R = \mu \frac{\ell}{voC_1{}^{(0)}} \chi g(\rho), \tag{13}$$

and

$$g(\rho) = \rho/(1 + \exp\ (a(\rho^* - \rho))). \tag{14}$$

Equation 14 is a modified step function. The advantage of a modified step function is its correct simulation of the concave variation of the outlet CO_2 concentration with time in the early stage of absorption. This behavior is typical of that reported by Bernard (2). The physical interpretation of equation 14 is that a sudden drop in reactivity of the absorbent occurs after a definite amount has been converted to Li_2CO_3, as is the case for LiOH absorbent. The parameters μ, a, and ρ^* are determined from a parametric analysis that yields the best agreement of predicted and measured CO_2 efflux from the canister.

A procedure was developed, and formulated as a Fortran computer program, to solve equations 4 and 5 under a variety of gas flow conditions. The model equations are coupled, nonlinear, partial differential equations. The numerical solution method adapted to solve the equations is a finite difference method (10). The particular finite difference method selected is implicit in time, except for the convective term in equation 4, which is treated explicitly. Forward time differencing and backward space differencing were used. This results in the replacement of the time derivatives of the form $\frac{\partial w}{\partial \tau}$ by

$$\frac{\partial w}{\partial \tau} = \frac{w^{n+1}(I) - w^n(I)}{\Delta \tau}, \tag{15}$$

where $\Delta\tau = \Delta t/t_1$ and Δt is the incremental time step between the value of w at the n+1st time step and the nth time step. The variable I refers to the Ith discrete location along the logitudinal direction in the absorbent, and w(I) is the value of the dependent variable w at location I. The spatial difference between adjacent grid locations is a constant Δx.

The spatial derivative is evaluated from a backward space difference approximation:

$$\frac{\partial w}{\partial \zeta} = \frac{w^n(I) - w(I-1)}{\Delta \zeta}, \tag{16}$$

where $\Delta\zeta = \Delta x/\ell$.

Equations 15 and 16 are first order accurate in $\Delta\tau$ and $\Delta\zeta$.

The finite difference representation of equations 4 and 5 with implementation of the difference expressions, equations 15 and 16, results in a total of 2N-1 algebraic equations, where N is the total number of spatial locations considered in the absorbent bed. Because of the terms that describe the absorption process, these equations are nonlinear. The finite difference representation of equation 5 is solved first for temporary values of ρ^{n+1} (I) using the

Newton-Rapheson method. There temporary values replace the values ρ^{n+1} (I) in equation 4. Equation 4 is then solved for χ^{n+1}. These values are substituted as temporary values in equation 5, and the process is repeated iteratively until numerical convergence is achieved. Then the values of χ and ρ at the nth time step are replaced by their new values, and the calculation is advanced in time. The procedure was developed into a Fortran computer program. To ensure numerical stability the time and space incremental steps were selected to satisfy the Courant-Friedrichs-Lewey condition (10).

APPLICATION

For the application considered in this report, it is assumed that the gas flow through the absorbent bed is represented by a modified sinusoidal traveling wave. The flow is unidirectional through the absorbent and occurs only during the exhalation segment of the breathing cycle. This constraint is formalized by a modification of a sinusoidal traveling wave in the specification of f(x,t) in equation 10. In particular,

$$f(x,t) = \sin(\omega(x/u_0 - t))h(t) \qquad (17)$$

$$h(t) = \begin{cases} 1, & \sin(\omega(x/u_0 - t)) > 0 \\ 0, & \sin(\omega(x/u_0 - t)) < 0 \end{cases} \qquad (18)$$

The angular frequency w is determined by the specified breathing rate, N.

$$\omega = \frac{2\pi N}{60} \qquad (19)$$

The amplitude, v_o, of the superficial velocity is determined from the volumetric flow rate, Q, and cross-sectional area, A, of the absorbent bed:

$$v_o = \frac{Q}{A}\frac{\pi}{60} \qquad (20)$$

Equation 20 was determined from the flow delivered in a single breathing cycle.

The flow rate and breathing rate, N, are related by the constraint that a constant tidal volume of 1.55 L is exchanged during each breath. This constraint was selected to be in accord with experiments reported for a Rescue-Pak scrubber (2).[3] The LiOH scrubber had a mass of 1.4 kg, a cross-sectional area of 178.5 cm^2, and a length of 20.5 cm. This represents a bulk density of 0.38 $g\cdot cm^{-3}$. The mass density of LiOH is 1.46 $g\cdot cm^{-3}$ (11), and the particle porosity is 0.5 (1). This defines a interstitial porosity of 0.46. The test conditions reported (2) for investigating the scrubber were inlet volumetric gas flow rates of 26, 37, and 48 L/min and an inlet CO_2 volumetric concentration of 3.5 pct. The CO_2 concentration measured in the air efflux from the canister was reported (2) for concentrations less than 0.9 pct. Discrete values (2) for flow rates of 26, 37, and 48 L/min are displayed in figure 2. Along with these measured values are shown predicted CO_2 efflux concentrations for the parameter set $a = 90$, $\mu = 7.5 \times 10^{-6}$, and $\rho^* = 0.05$. These values were determined to be the best values on a trial and error basis. The agreement between measured and predicted effluent CO_2 concentrations is reasonable. The predicted values of CO_2 efflux shown in the figures of this report are in each case the maximum value that occurs during a single breath. The results in figure 2 are in the time regime prior to the depletion of the absorbent such that ρ is less than ρ^* (see equation 14) for a significant region of the absorbent bed. The long time effect of the absorption process is for the effluent concentration curve to undergo an inflection and reach as an asymptotic value the inlet CO_2 concentration. This long time effect for a 20.5-cm bed of LiOH is shown in figure 3.

The effect of bed length on CO_2 absorption with the constraint of constant porosity, which has a value of 0.46, was analyzed for bed lengths of 15.375, 20.5, and 25.625 cm. In each case the flow rate of 48 L/min was maintained. The

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

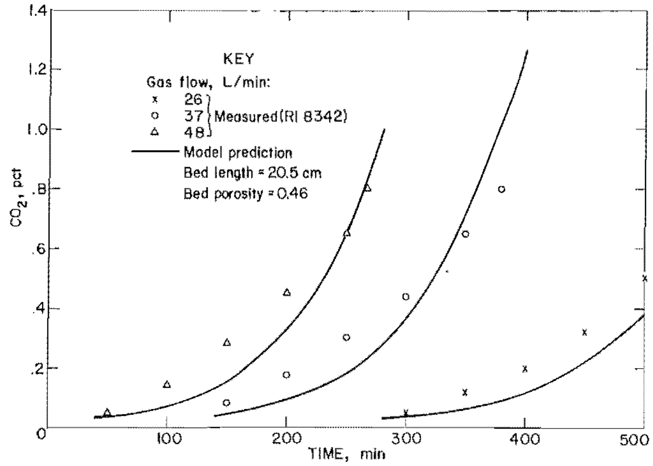

FIGURE 2.—Measured and predicted CO_2 effluent concentration for flows of 26, 37, and 48 L/min.

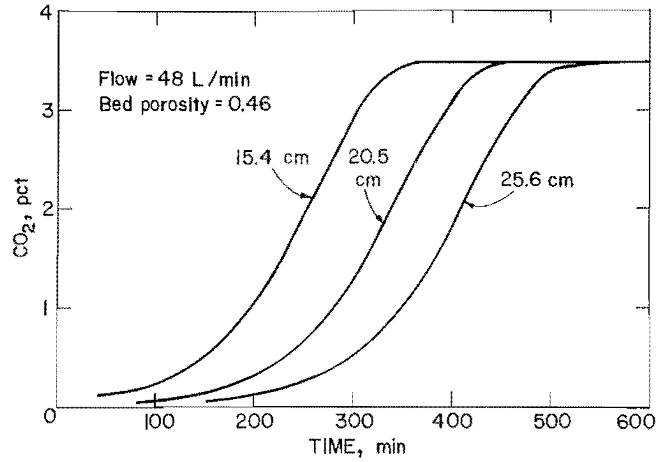

FIGURE 4.—Predicted effluent CO_2 concentration for bed lengths of 15.4, 20.5, and 25.6 cm.

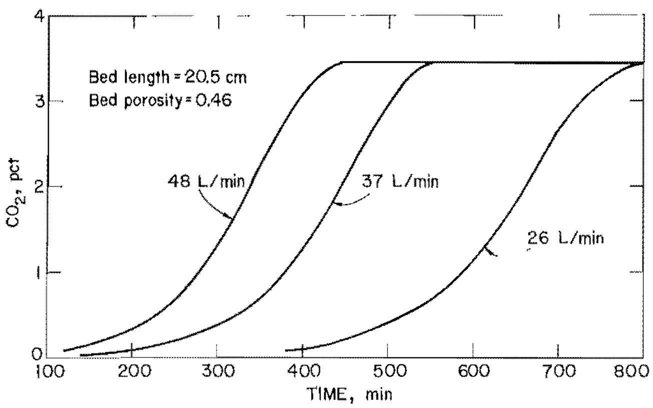

FIGURE 3.—Predicted effluent CO_2 concentrations for gas flows of 26, 37, and 48 L/min.

constraint of constant porosity was satisfied through a linear variation in the mass of LiOH in direct proportion to the bed length. The predicted effluent CO_2 concentrations from the absorbent bed are shown in figure 4. It is observed that the time required for the CO_2 concentration to attain a prescribed value is directly proportional to the bed length. The 15.375-cm bed has a void volume that is less than the tidal volume (1.55 L), whereas the remaining two bed lengths have a void volume greater than the tidal volume. According to Adriani and Byrd (12) the absorption process is at maximum efficiency when the tidal volume equals the displaceable air space. Figure 4 indicates that the time to breakthrough is expected to vary linearly with the length on either side of the length corresponding to the case where displaceable airspace equals the tidal volume, and the Adriani-Byrd result does not appear to be important for this aspect of canister design. In any event, as pointed out by Kyriazi (13), the tidal volume will change with work rate.

The effect of gas flow rate upon bed absorption for fixed bed length and constant porosity was analyzed with the model. The bed length was 20.5 cm, the porosity was equal to 0.46, and flow rates of 26, 37, and 48 L/min were considered. The CO_2 concentration of the effluent gas is shown in figure 3 for time less than 800 min. It was determined that the time for the CO_2 efflux to attain a specified value is inversely proportional to the gas flow rate.

The computations discussed above were for a constant interparticle porosity of 0.46. This physical property is strongly subject to design considerations. In particular, the pellet size of the absorbent and the packing of the pellets will affect the porosity value. The influence of porosity on breakthrough time was evaluated for a fixed bed length, 20.5 cm, of LiOH through a variation of the mass of the LiOH. The gas flow rate was maintained at 48 L/min.

Figure 5 shows the predicted CO_2 efflux for porosities of 0.46, 0.60, and 0.65. A regression analysis of the time for breakthrough versus the porosity shows that the time for breakthrough is proportional to $\varepsilon^{-1.5}$.

Boryta and Maas (6) identified the ratio ℓ/Q as important for defining the breakthrough time in their study of CO_2 absorption by LiOH. This model shows that the breakthrough time is proportional to $\ell/(Q\varepsilon^{1.5})$. The normalized absorbent concentration, ρ, is determined as a solution to equations 4 and 5. This quantity decreases with depth into the bed as additional CO_2 is transported through the bed and depleted through chemical reaction.

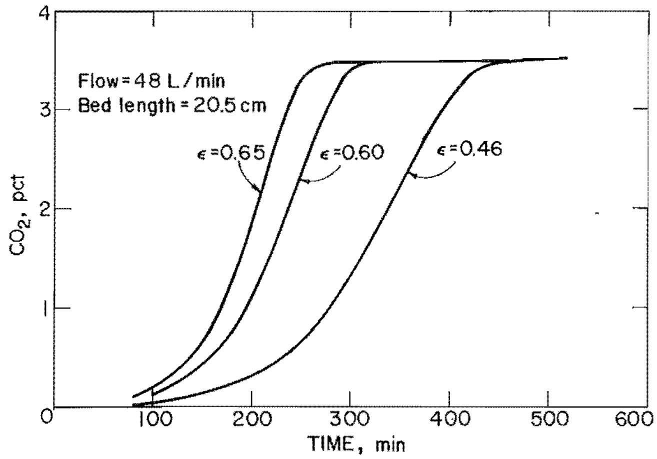

FIGURE 5.—Predicted effluent CO_2 concentrations for bed porosities (ϵ) of 0.46, 0.60, and 0.65.

CONCLUSIONS

A mathematical model (5) with three adjustable parameters that describes the removal of CO_2 from a gas stream passing in a unidirectional mode through a bed of absorbent was extended to include a variable gas velocity. The mathematical complexity of the model required a numerical solution. The solution procedure was formulated as a Fortran computer program. The model was applied to an analysis of the effluent CO_2 from a bed of LiOH and showed relatively good agreement with measured values reported elsewhere (2). Based upon the parameters selected to model the measured results, a parametric study was made with regard to bed length, flow velocity and bed porosity. The parametric analysis showed the breakthrough time of the CO_2 efflux to be directly proportional to the bed length, inversely proportional to the gas flow rate, and inversely proportional to the interparticle porosity raised to the 1.5 power. For a canister with a specified cross section and an absorbent bed with a fixed interparticle porosity, the model can be used to determine the minimum length of absorbent bed required to prevent the efflux of CO_2 above a prescribed threshold under a variety of gas flow conditions. This is equivalent to stating that the amount of absorbent required to maintain the CO_2 efflux below a threshold value for a specified time can be determined with the model.

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APPENDIX.--NOMENCLATURE

a	coefficient in absorption term, $cm^3 \cdot mol^{-1}$
A	Absorbent bed cross-sectional area, cm^2
C_1	molar concentration of CO_2, $mol \cdot cm^{-3}$
C_2	molar concentration of LiOH, $mol \cdot cm^{-3}$
$C_1^{(0)}$	CO_2 concentration at bed entrance, $mol \cdot cm^{-3}$
$C_2^{(0)}$	initial LiOH concentration, $mol \cdot cm^{-3}$
ℓ	LiOH bed length, cm
N	breathing rate, bpm
Q	gas volumetric flow rate, cm^3/min
r_1	absorption rate of CO_2, $mol \cdot cm^{-3} \cdot s^{-1}$
r_2	reaction rate of absorbent, $mol \cdot cm^{-3} \cdot s^{-1}$
t	time, s
u	interstitial gas velosity, $cm \cdot s^{-1}$
v	superficial gas velocity, $cm \cdot s^{-1}$
Vo	amplitude of V, $cm \cdot s^{-1}$
W^n (I)	value of dependent variable W
x	distance from entrance of absorbent bed, cm
$\Delta\zeta$	incremental value of ζ, 1
$\Delta\tau$	incremental value of τ, 1
ε	bed porosity, 1
ζ	normalized distance into absorbent bed, 1
μ	coefficient in absorption term, $cm^3 \cdot s \cdot mol^{-1}$
π	pi, equals 3.14159
ρ	C_2 normalized by $C_2^{(0)}$, 1
ρ^*	coefficient in absorption term, $mol \cdot cm^{-3}$
τ	normalized time, 1
χ	C_1, normalized by $C_1^{(0)}$, 1
ω	angular frequency, $rad \cdot s^{-1}$

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